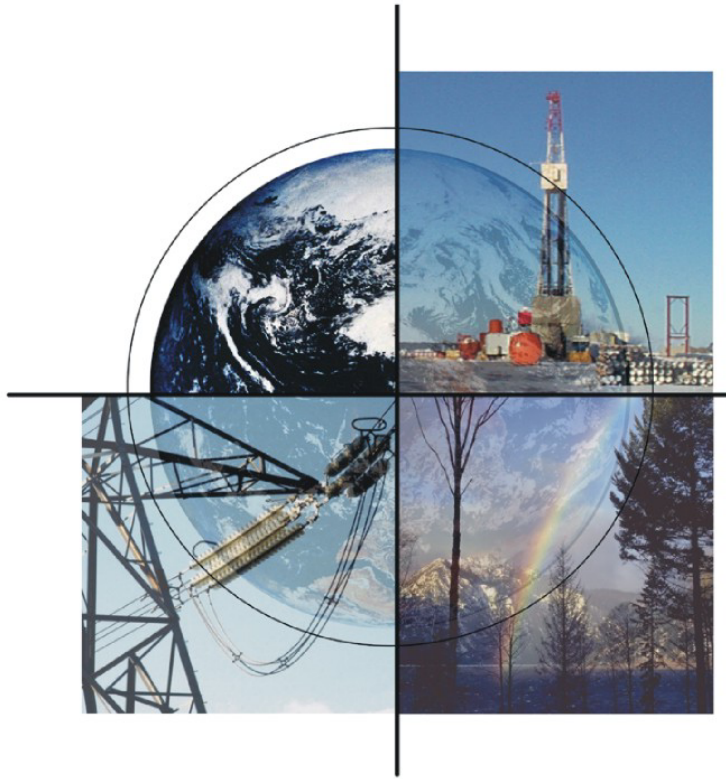


# Systems Analysis of CO<sub>2</sub> Capture Concepts



Tom Tarka (Energetics)  
Phil DiPietro (Energetics)  
Jared Ciferno (NETL)

**Presentation at the NETL Peer Review, 06/23/04**



# Goals and Objectives

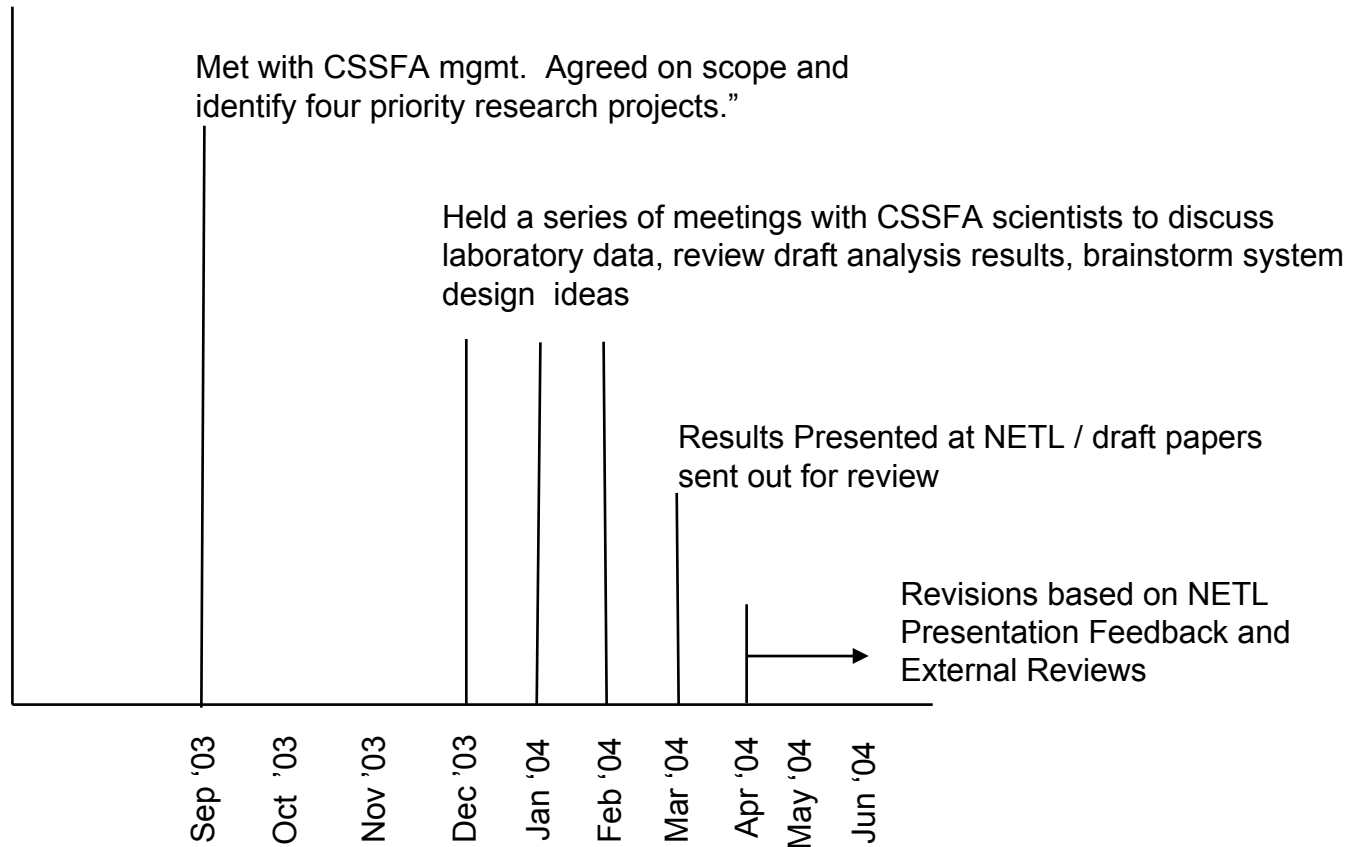
- **Place R & D work in a systems context**
- **Assess potential of research projects to meet the program goals**
- **Craft a paper and presentation materials to summarize results and detail methodology**

# Scope of Work

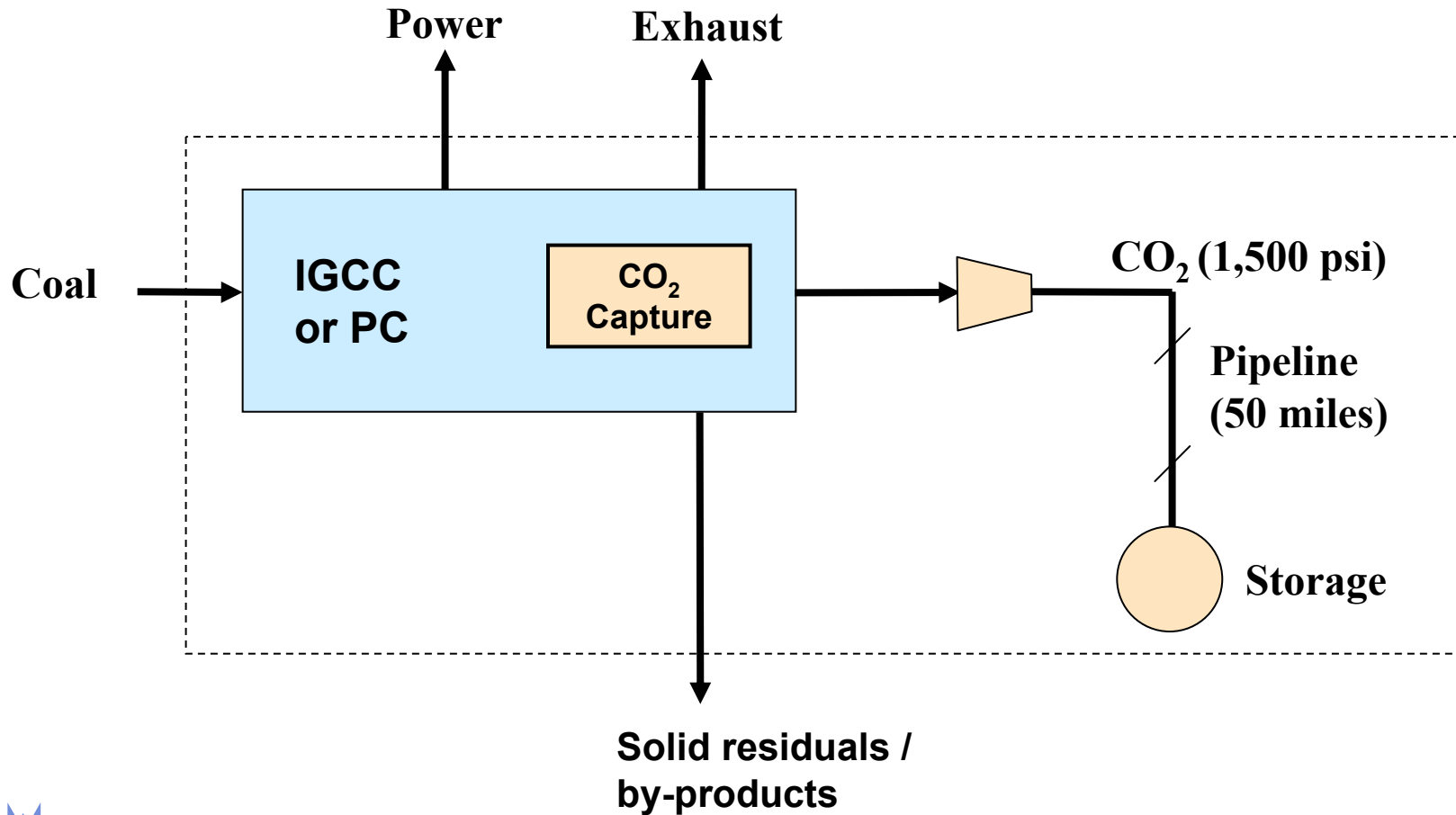
- **Assess four capture technologies in FY04**
  - Aqueous Ammonia
  - Organosilane hybrid membrane
  - Aminated Sorbents
  - Lithium sorbents
- **Level of effort is roughly 1.25 FTE**
  - 0.25 of Jared Ciferno
  - 0.25 of Phil DiPietro
  - 0.75 of Tom Tarka



# Work Time Line



# Analysis Boundary



# Analysis Process

- 1. Interview researchers / review literature**
- 2. Develop conceptual design(s)**
- 3. Perform mass and energy balances to 400 MW net gen**
- 4. Estimate equipment cost, system efficiency, and rates pollutant emission and by-product generation**
- 5. Develop a cash flow model of a power plant with the capture system**
- 6. Exercise the model to quantify sensitivities**
- 7. Compare and contrast technology performance with**
  - Base case power plant without capture
  - Base case power plant with commercially-available capture
- 8. Provide recommendations**
- 9. Iterate with researchers, identify optimal systems design**
- 10. Send vetted analysis for external review**



# Performance Metrics

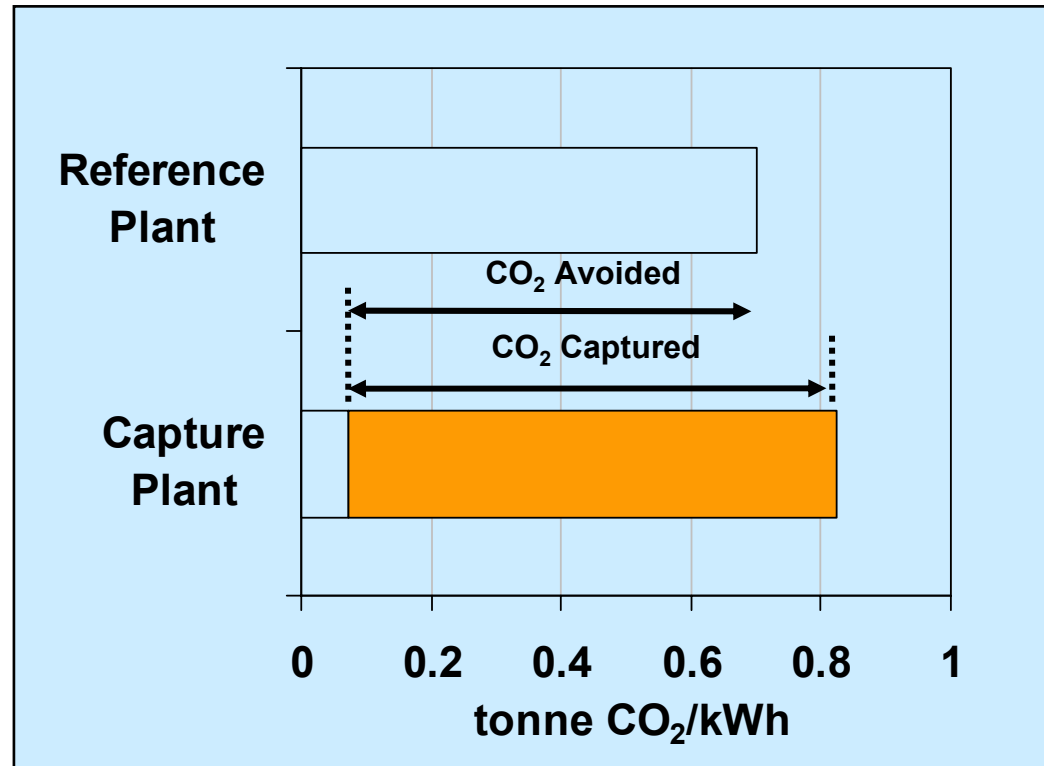
## Cost of Avoided Emissions

$\Delta\text{COE} / \Delta\text{Carbon Intensity}$

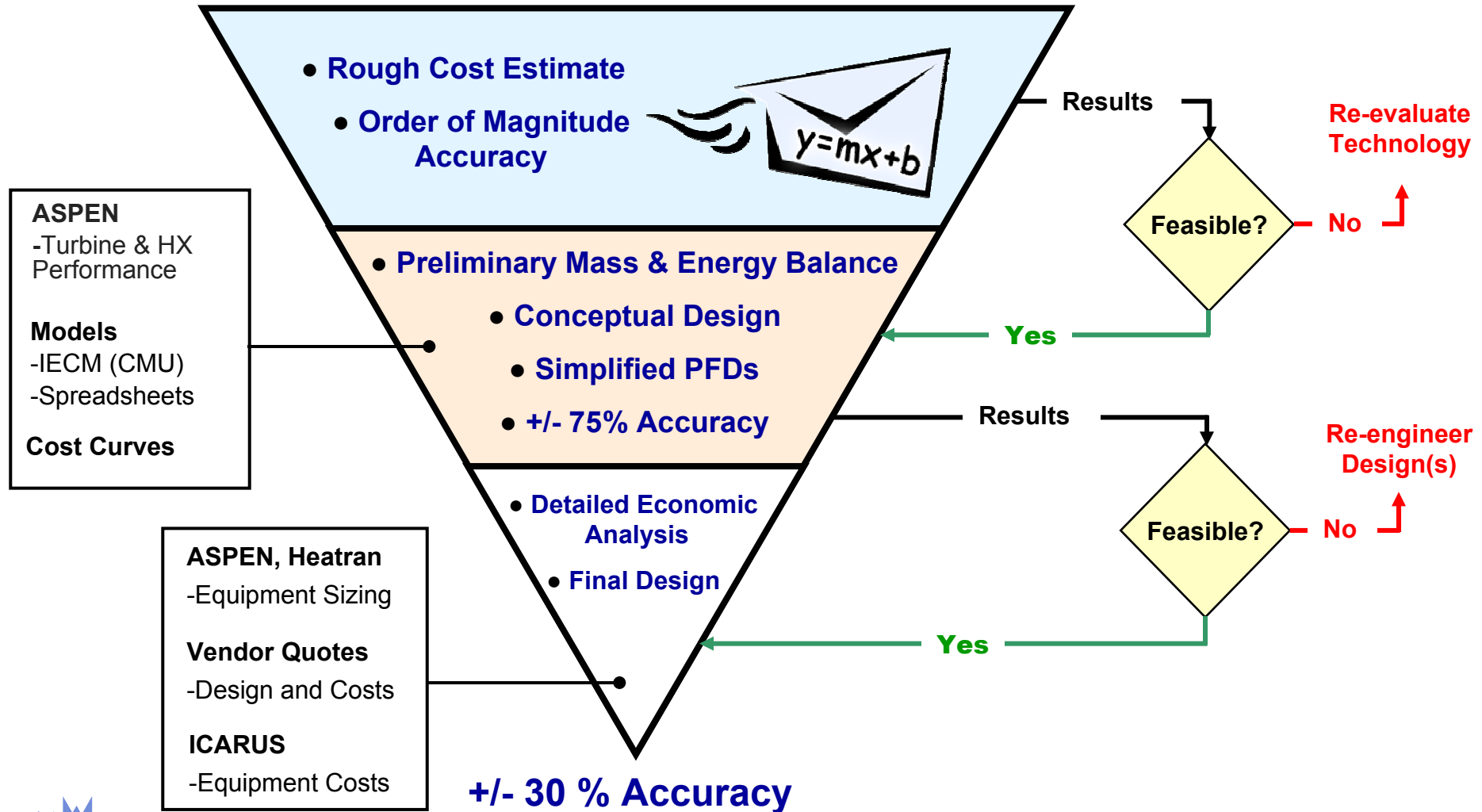
$$\frac{(c/\text{kWh}_{\text{capture}} - c/\text{kWh}_{\text{base}})}{(\text{kgC}/\text{kWh}_{\text{base}} - \text{kgC}/\text{kWh}_{\text{capture}})}$$

## Percent increase in COE

$$(c/\text{kWh}_{\text{capture}} / c/\text{kWh}_{\text{base}}) - 1$$



# Approach



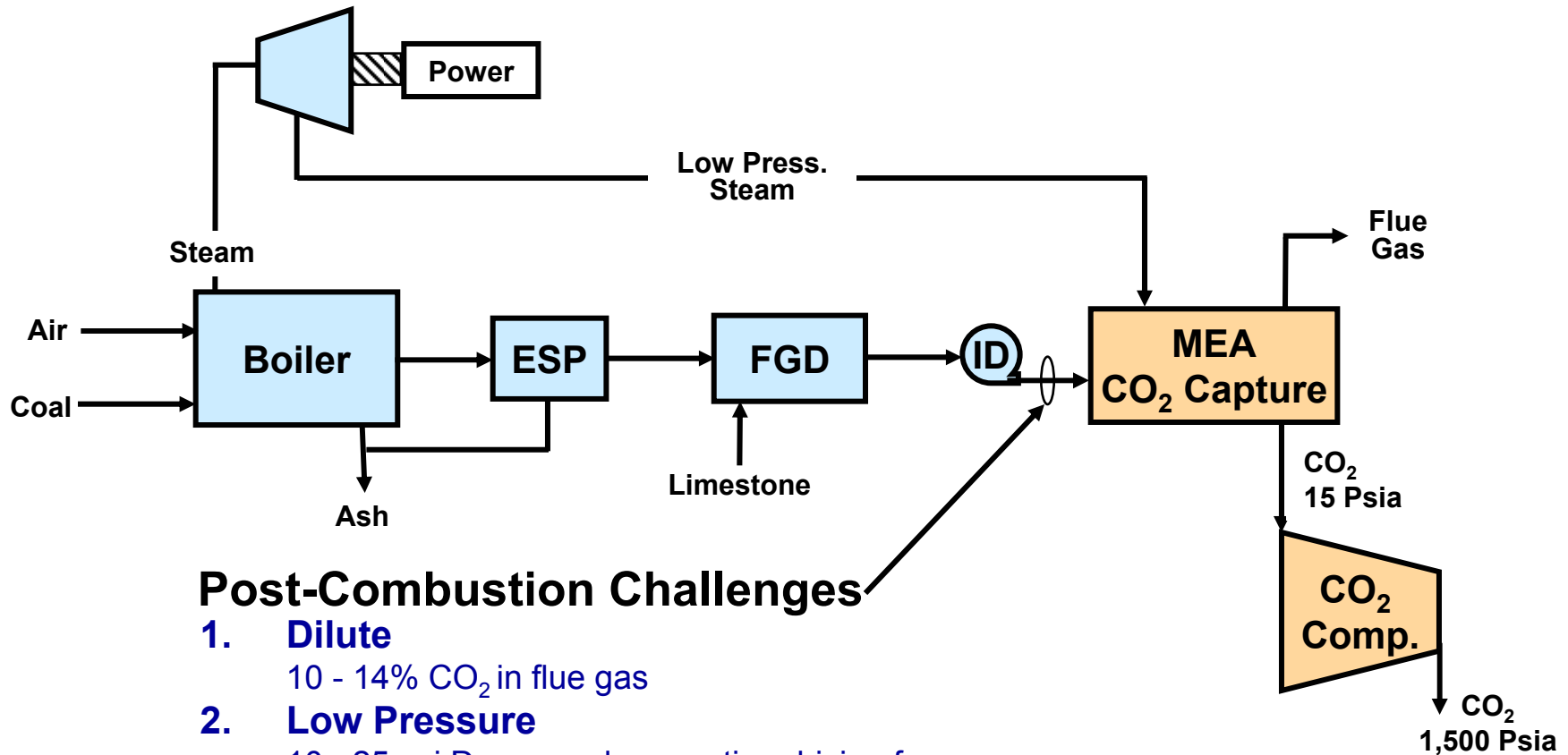


# Pulverized Coal Base Case



# Post-Combustion Current Technology

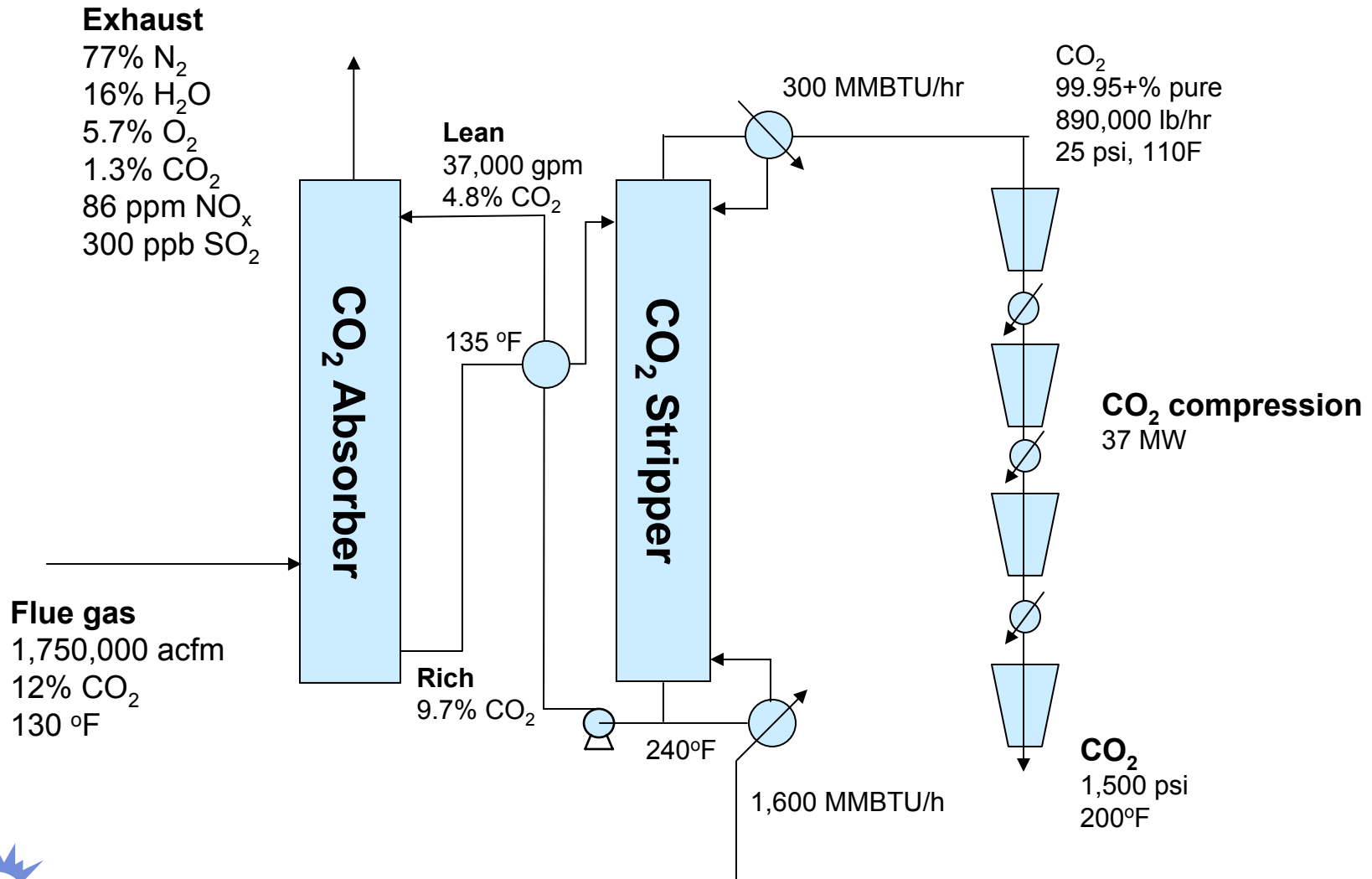
## *Pulverized Coal Power Plant with CO<sub>2</sub> Scrubbing*



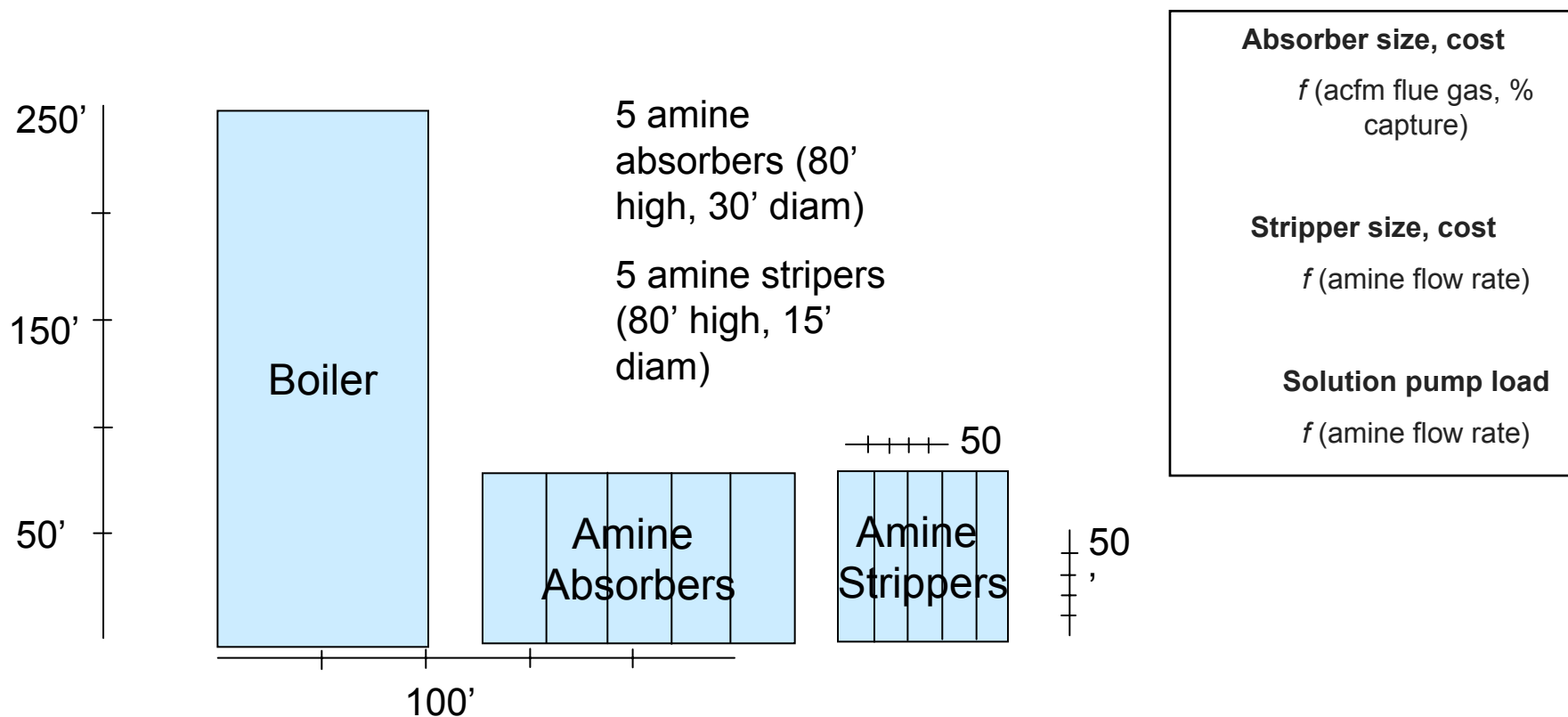
### Post-Combustion Challenges

1. **Dilute**  
10 - 14% CO<sub>2</sub> in flue gas
2. **Low Pressure**  
10 - 25 psi Decreased separation driving force
3. **Contaminants**  
SO<sub>2</sub>, SO<sub>3</sub>, Particulates, etc.

# Amine-based CO<sub>2</sub> Capture System



# Amine Plant Size and Cost



# Amine make-up cost

- **5 kg MEA / mt CO<sub>2</sub> absorbed**
  - General loss: 1.6 kg MEA/mt CO<sub>2</sub>
  - SO<sub>x</sub> loss: 2 mole MEA/mole SO<sub>x</sub> in absorber inlet
- **Amine cost \$1.50 per kg**
  - Econoamine, includes inhibitor cost
- **Cost equals 7.5 \$/mt CO<sub>2</sub> captured**
  - 5 kg MEA / mt CO<sub>2</sub> \* \$1.50/kg MEA

Amine make-up rate from “recovery of CO<sub>2</sub> from flue gases: Commercial Trends, G. Chapel, C. Mariz, J. Ernst, 1999;



## PC Base Case Economic Results

	No CO <sub>2</sub> Capture	Amine Capture
Gross Power (MW)	425	503
Heat Rate (Btu/kWh)	8,500	9,900
\$/kW (equipment)	1,100	1,900
\$/kW (contingency)	400	700
COE (cents/kWh)	4.9	9.0
CO <sub>2</sub> intensity (kg/kWh)	0.76	0.112
% increase in COE	N/A	84%
Avoided cost (\$/mtCO <sub>2</sub> )	N/A	63

# Aqueous Ammonia for CO<sub>2</sub> Capture

# Use of Aqueous Ammonia for SO<sub>2</sub> Capture is a Commercially Available Technology

- **ALSTOM Power offers Ammonia Scrubbing as one of its SO<sub>2</sub> compliance options**
  - 130 MW demonstration at First Energy's Niles plant in Ohio
  - By-product revenue drive economics
- **Idea for this project is to add CO<sub>2</sub> capture**

	Limestone Scrubber	Aqueous Ammonia
<b>Parasitic Load (MW)</b>	<b>4-7</b>	<b>0.2</b>
<b>Reactant cost (\$/ ton SO<sub>2</sub>)</b>	<b>22</b>	<b>109</b>
<b>By-product revenue (\$/ton SO<sub>2</sub>)</b>	<b>0</b>	<b>217</b>
<b>Net material revenue (\$/ton SO<sub>2</sub>)</b>	<b>(22)</b>	<b>+108</b>
Limestone 15 \$/ton, anhydrous ammonia 200 \$/ton, no pay market for FGD sludge, ammonia sulfate 105 \$/ton		



# Aqueous Ammonia for CO<sub>2</sub> Capture from PC Power Plants

Similar to aqueous amines (liquid chemical absorbent that uses steam to regenerate) with 4 hooks

1. Reduced steam load
2. More concentrated CO<sub>2</sub> carrier
3. Lower-cost chemical
4. Multi-pollutant control with salable by-products



# Hook 1: Reduced Steam Load

$$Q_{\text{regen}} = Q_{\text{rxn}} + Q_{\text{sensible}} + Q_{\text{strip}}$$

- **Q reaction**

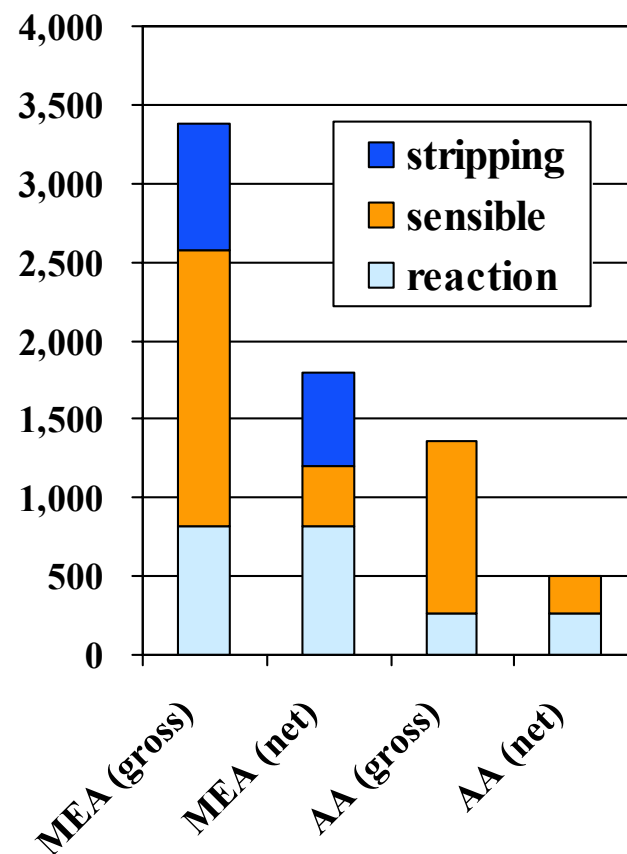
- MEA: 825 BTU/lb CO<sub>2</sub> captured
- AA: 262 Btu/lb CO<sub>2</sub> (carbonate/bicarb)

- **Q sensible**

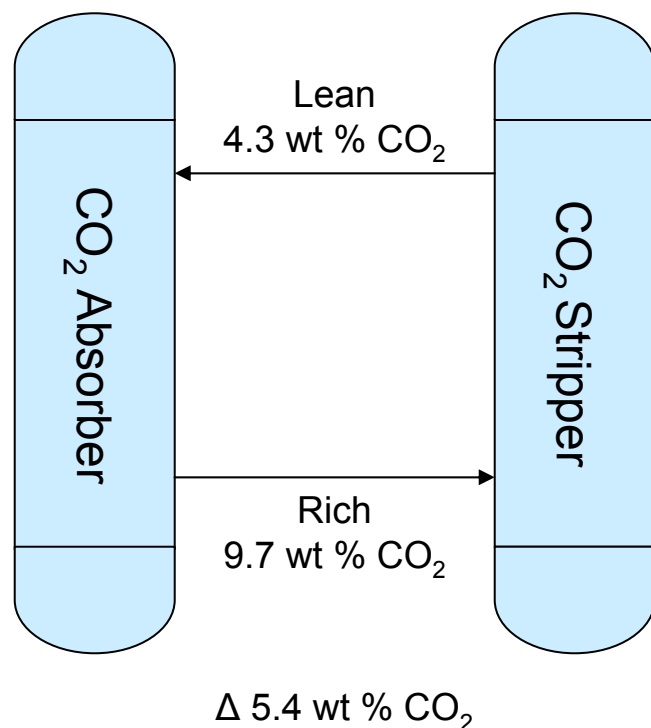
- MEA: (135F-240F)\*18.5 lbs sol./lb CO<sub>2</sub> \* 0.9 Btu/lbF  
= 1,750 Btu/lb CO<sub>2</sub>
- AA: (80F) \* 14.7 lbs sol./lb CO<sub>2</sub> \* 0.9 Btu/lbF  
= 1,100 Btu/lb CO<sub>2</sub>

- **Q stripping**

- MEA: 800 Btu/lb CO<sub>2</sub> (1 mole steam per mole CO<sub>2</sub>)
- AA: assume no stripping steam required



## Hook 2: Reduced sorbent solution flowrate



Laboratory results indicate

Aqueous Ammonia can

achieve a loading difference  
of 6.8 wt % CO<sub>2</sub>

- reduces stripper cost  
from 36.4 to 25.2 MM\$
- reduced circulation pump  
load from 1.8 to 1.2

$$\text{MEA Solution flowrate} = \frac{12,000 \text{ ton CO}_2/\text{day}}{.054} = 220,000 \text{ ton/day}$$

## Hook 3: Lower cost chemical

- Cost of MEA
  - $\$1.50/\text{kg MEA} * 0.3 \text{ kg MEA/kg soln.} * 18.5 \text{ kg soln./kg CO}_2$   
**= \$8.33 / kg CO<sub>2</sub> carrying capacity**
- Cost of Ammonia\*
  - $\$0.20/\text{kg Amm.} * 0.15 \text{ kg Amm/kg soln.} * 14.7 \text{ kg soln./kg CO}_2$   
**= \$0.44/kg CO<sub>2</sub> carrying capacity**

\* Anhydrous Ammonia cost, cost of aqueous ammonia is roughly 4x. Cost of bicarbonate 30% increase



# Chemical Make-up cost

- AA loss: 4.4 kg AA / mt CO<sub>2</sub>
  - General use: 2 kg AA / mt CO<sub>2</sub>
    - Conservatively high based on amine heuristic
  - SO<sub>2</sub>: 2.4 kg AA / mt CO<sub>2</sub>
    - 2 NH<sub>3</sub>/SO<sub>2</sub> --- 34/64, 0.53 tons Ammonia / tons SO<sub>2</sub>
    - (1.33 + 0.046)mt SO<sub>2</sub> / 400 MWh \* 1,000 kg SO<sub>2</sub>/mt = 0.00344 kg SO<sub>2</sub>/kWh (CO<sub>2</sub> absorber inlet)
    - 0.00344 kg SO<sub>2</sub>/kWh \* 0.53 kg AA/kg SO<sub>2</sub> \* 1kWh/(1.7 lbs CO<sub>2</sub> /2200 lbs/mt) = 2.4 kg AA / mt CO<sub>2</sub>
- AA makeup cost: \$0.88 / mt CO<sub>2</sub> captured
  - \$0.20/kg AA \* 4.4 kg AA/mt CO<sub>2</sub> = \$ 0.88 mt CO<sub>2</sub>
- Low compared to MEA cost of \$7.5 / mt CO<sub>2</sub>

## Hook 4: Value-added by products

- $\text{SO}_2 \rightarrow (\text{NH}_4)_2\text{SO}_4$  (Ammonium Sulfate Fertilizer)
- $\text{NO}_x \rightarrow (\text{NH}_4)\text{NO}_3$  (Ammonium Nitrate Fertilizer)
- $\text{Hg} \rightarrow$  oxidized solid

# By-product Revenues Summary Table

	Production Rate (lb/kWh)	Value (\$/ton)	Op. cost (\$/ton)	Op. revenue (\$/ton)	Norm. Rev. (\$/ton CO <sub>2</sub> )
Mercury	$7 \times 10^{-8}$	$1.2 \times 10^8$	0	$1.2 \times 10^8$	4.9
Ammonium Nitrate	0.010	155	218	(62.5)	(.36)
Ammonium Sulfate	0.068	105	51	54	2.9*
CO <sub>2</sub>	1.7	--	--	--	--
*Includes value of avoided parasitic load from the limestone scrubber of 4 MW (\$ 0.81/ton CO <sub>2</sub> )					

# Ammonium Sulfate

## Data

- Ammonia cost, 200 \$/ton (Anhydrous, Chemical Marketing Reporter)
- Market value of ammonium sulfate, 105 \$/ton (Chemical Marketing Reporter)
- 2.5 wt% sulfur in coal, heat content 12,760 Btu/lb
- 8,500 Btu/lb heat rate
- $\text{SO}_2 + 2\text{NH}_3 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$
- 5 MW load associated with a limestone scrubber for a 400 MW PC power plant

## Calculations

- Ammonia use:  $2 \text{ NH}_3 / \text{SO}_2 \rightarrow 34/64$ , 0.53 tons Ammonia / tons  $\text{SO}_2$
- Fertilizer generation rate:  $\text{SO}_2 / (\text{NH}_4)_2\text{SO}_4 \rightarrow 64/132 = 0.485 \text{ ton SO}_2 / \text{ton fertilizer}$
- Fertilizer feedstock cost:  $200 \text{ $/ton Amm} * 0.53 \text{ Amm/SO}_2 * 0.485 \text{ SO}_2/\text{fertilizer} = 51.4 \text{ $/ton}$
- Fertilizer operating revenue:  $105 - 51.4$ , 53.6 \$/ton fertilizer
- $(8,500 \text{ Btu/kWh} / 12,760 \text{ Btu/lb}) * 0.025 \text{ lbS/lb coal} * 2 \text{ lb SO}_2/\text{lb S} = 0.033 \text{ lb SO}_2/\text{kWh}$
- $(8,500 \text{ Btu/KWh} / 12,760 \text{ Btu/lb}) * 0.71 \text{ lbC/lb coal} * 3.67 \text{ lb CO}_2/\text{lb C} = 1.73 \text{ lb CO}_2/\text{kWh}$
- $0.033 \text{ lb SO}_2/\text{kWh} / 0.485 \text{ lbs SO}_2/\text{lb fertilizer} = 0.068 \text{ lbs fertilizer generated per kWh}$
- **$\$53.6 / \text{ton fertilizer} * (0.068/1.73) = \$ 2.1 \text{ of fertilizer revenue per ton CO}_2$**
- $(5/400) \text{ kWh/kWh} * \$0.05/\text{kWh} * 1 \text{ kWh}/(1.7 \text{ lbs CO}_2 * 2000 \text{ lbs/ton}) = \$0.81 / \text{tonCO}_2$





# Ammonium Nitrate

## Data

- Ammonia cost, 200 \$/ton (Anhydrous, Chemical marketing Reporter)
- Market value of ammonium nitrate, 155 \$/ton (Chemical Marketing Reporter)
- Ozone cost: 450 \$/ton
- $\text{NO}_x \rightarrow \text{NO}_3; \text{NO}_3 + \text{NH}_4 \rightarrow (\text{NH}_4)\text{NO}_3$

## Calculations

- Ammonia use:  $\text{NH}_4/\text{NO} \rightarrow 18/30$ , 0.6 tons Ammonia / tons  $\text{NO}_x$
- Fertilizer generation rate:  $\text{NO}_x / (\text{NH}_4)\text{NO}_3 \rightarrow 30/80 = 0.375$  ton  $\text{NO}_x$  / ton fertilizer
- Fertilizer feedstock cost:  $200 \text{ \$/ton Amm} * 0.6 \text{ Amm/NO}_x * 0.375 \text{ NO}_x/\text{fertilizer} = 45 \text{ \$/ton}$
- Ozone feedstock cost:  $\$460/\text{ton NO}_x * (30/80) = 172.5 \text{ \$/ton fertilizer}$
- Fertilizer operating revenue:  $155 - (45 + 172.5) = -62.5 \text{ \$/ton fertilizer}$
- $(8,500 \text{ Btu/KWh} / 12,760 \text{ Btu/lb}) * 0.71 \text{ lbC/lb coal} * 3.67 \text{ lb CO}_2/\text{lb C} = 1.73 \text{ lb CO}_2/\text{kWh}$
- $0.0038 \text{ lb NO}_x/\text{kWh} / 0.375 \text{ lbs SO}_2/\text{lb fertilizer} = 0.010 \text{ lbs fertilizer generated per kWh}$
- **$(\$62.5)/\text{ton fertilizer} * (0.010/1.73) = (\$ 0.36) \text{ fertilizer revenue per ton CO}_2$**



# Mercury

## Data:

- 8.2 lbs mercury per trillion Btu coal (0.2 lbs Hg per thousand short tons of coal)\*
- Estimated value of mercury emissions reduction: 60,000 \$/lb Hg [FE website]

## Calculations:

- Mercury generation rate:  $(8,500 \text{ Btu/KWh} * 8.2 \text{ lbs Hg} / 10^{12} \text{ Btu coal} = 7 \times 10^{-8} \text{ lb Hg/kWh}$
- $60,000 \text{ $/lb} * 7 \times 10^{-8} \text{ lb Hg/kWh} = \$0.0042 \text{ $/kWh}$
- $\$0.0042/\text{kWh} * 1 \text{ kWh} / 1.7 \text{ lbs CO}_2 * 2000 \text{ lb /ton} = 4.9 \text{ $/ton CO}_2$

\* EIA, "Analysis of Strategies for Reducing Multiple Emissions from Electric Power Plants: Sulfur Dioxide, Nitrogen Oxides, Carbon Dioxide, and Mercury and a Renewable Portfolio Standard, July 2001

# Ammonia Sulfate Market Size

	Million tons per year
Ammonia sulfate generated from one 400 MW PC power plant (2.5% S coal)	.073
Current domestic market for ammonium sulfate	2
Current world demand for nitrogen fertilizer	83

$(9,100 \text{ Btu/kWh} / 12,760 \text{ Btu/lb}) * 0.025 \text{ lbS/lb coal} * (114/32 \text{ lbs AS/lb S}) = 0.064 \text{ lbs AS/kWh}$

$400,000 \text{ kW} * (0.65 * 8,760) \text{ hr/yr} * 0.064 \text{ lbs AS/kWh} * 0.0005 \text{ tons/lb} = 73,000 \text{ tons AS/yr}$



<b>Metric</b>	<b>Base</b>	<b>Amine</b>	<b>AA (CO<sub>2</sub> only)</b>	<b>AA (CO<sub>2</sub> and SO<sub>2</sub>)</b>	<b>AA (CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, Hg)</b>
Boiler turbine cap cost, \$/kW	830	830	830	830	830
Gross Power, MW	425	503	494	492	492
CO <sub>2</sub> capture cap cost, \$/kg CO <sub>2</sub> /hr	N/A	350	320	320	320
Steam to CO <sub>2</sub> rec. (Btu/ kg CO <sub>2</sub> )		6,000	1,700	1,700	1,700
CO <sub>2</sub> comp. load (kWh/kg CO <sub>2</sub> )		0.15	0.14	0.14	0.14
By-product revenue, cents/kWh		0	0	0.36	0.81
Percent increase in COE		84	50	31	21
Capture cost per mt CO <sub>2</sub> avoided		63	37	28	21

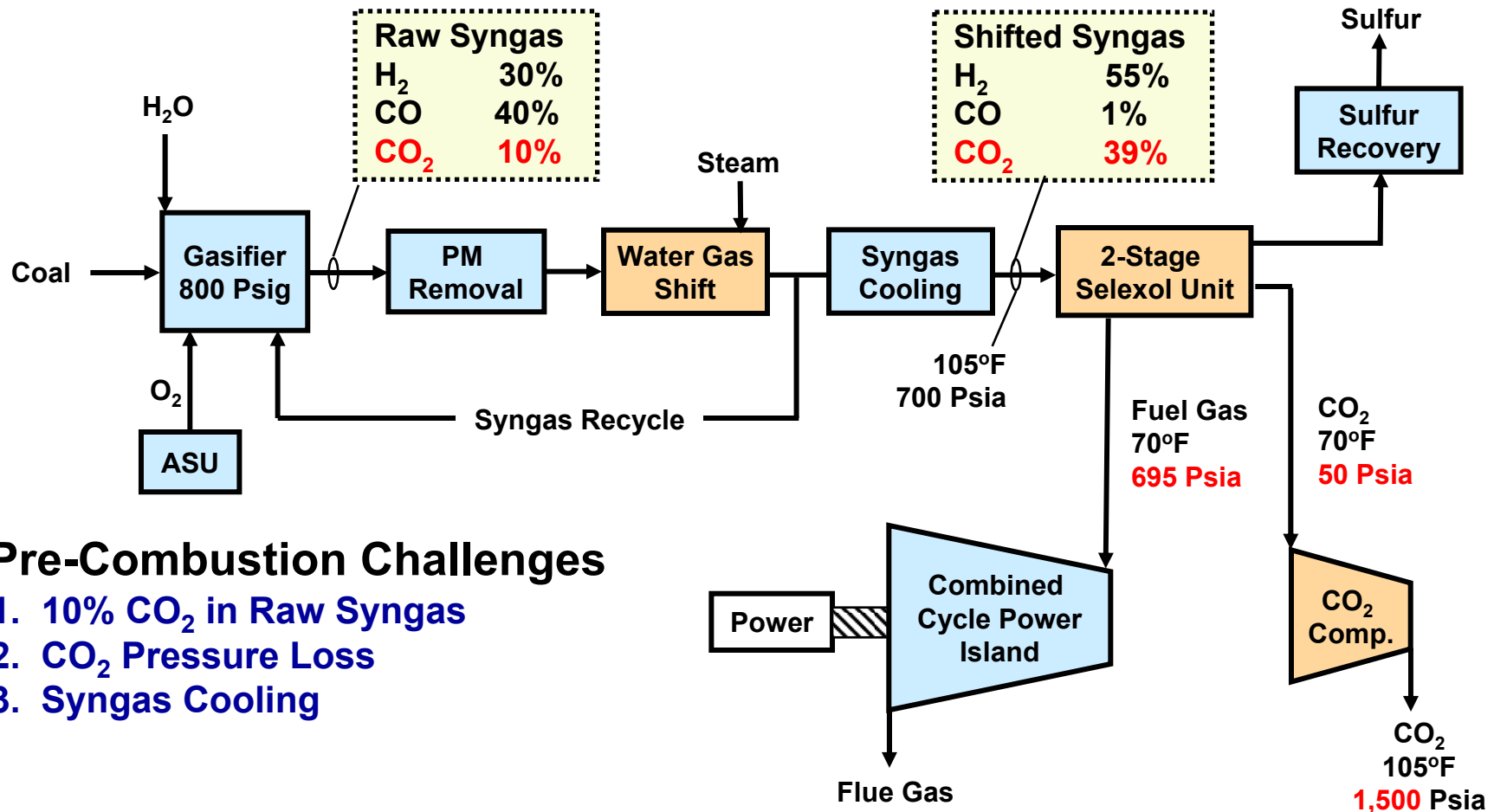
# Future Analysis Work for this Technology

- More rigorous market study of ammonia sulfate/nitrate
  - International markets
  - Competing commodities,
  - Reliance on natural gas
- Evaluate trade-offs between absorption/desorption temperatures and CO<sub>2</sub> transfer capacity
  - Possible need for flue gas cooling
- Closer look at ammonia slip
  - Tailgas cleanup / guard options
  - Use of bicarbonate as feedstock
- Closer look at heat integration and stripping steam requirements

# **CO<sub>2</sub> Capture from IGCC Base Case**

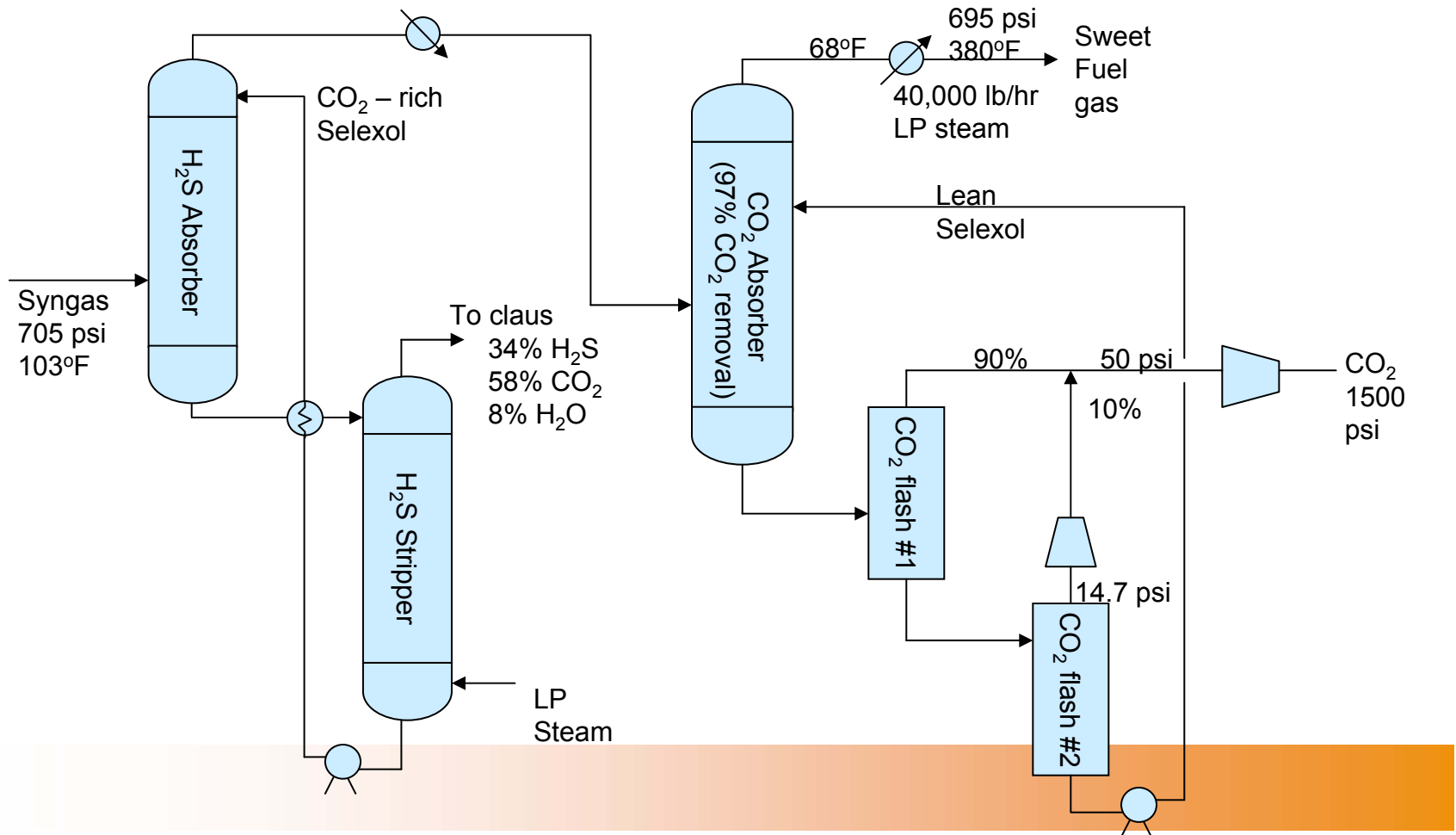
# Pre-Combustion Current Technology

## IGCC Power Plant with CO<sub>2</sub> Scrubbing



Source: *Evaluation of Innovative Fossil Fuel Power Plants with CO<sub>2</sub> Removal*, DOE/EPRI, 1000316

# Selexol combined H<sub>2</sub>S/CO<sub>2</sub> capture system, simplified PFD

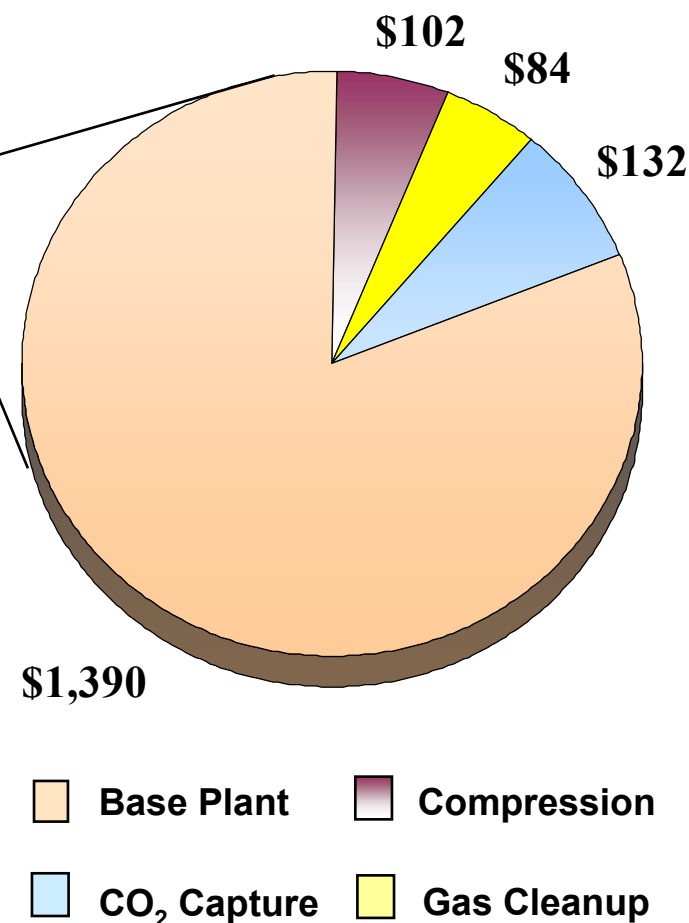




# IGCC with CO<sub>2</sub> Capture Base Case Results

	No Capture	Capture
Total Power Plant Capital (\$/kWh)	1,430	1,707
Capital COE (c/kWh)	3.73	4.43
Variable COE (c/kWh)	1.78	2.07
Total COE (c/kWh)	5.51	6.50
Including Transportation and Storage		
Total Capital (\$/kWh)	1,430	1,838
Total \$/tonne CO <sub>2</sub> avoided	-	23.30
Total Sequestration COE (c/kWh)	-	6.87
Increase in COE (%)	-	25%
*No Capture Case Includes MDEA H <sub>2</sub> S Removal		

Based On: 1,500Ft Saline Aquifer, Levelized COE 15%, 65%  
Capacity Factor, 50 Mile Pipeline, 2002 Dollars

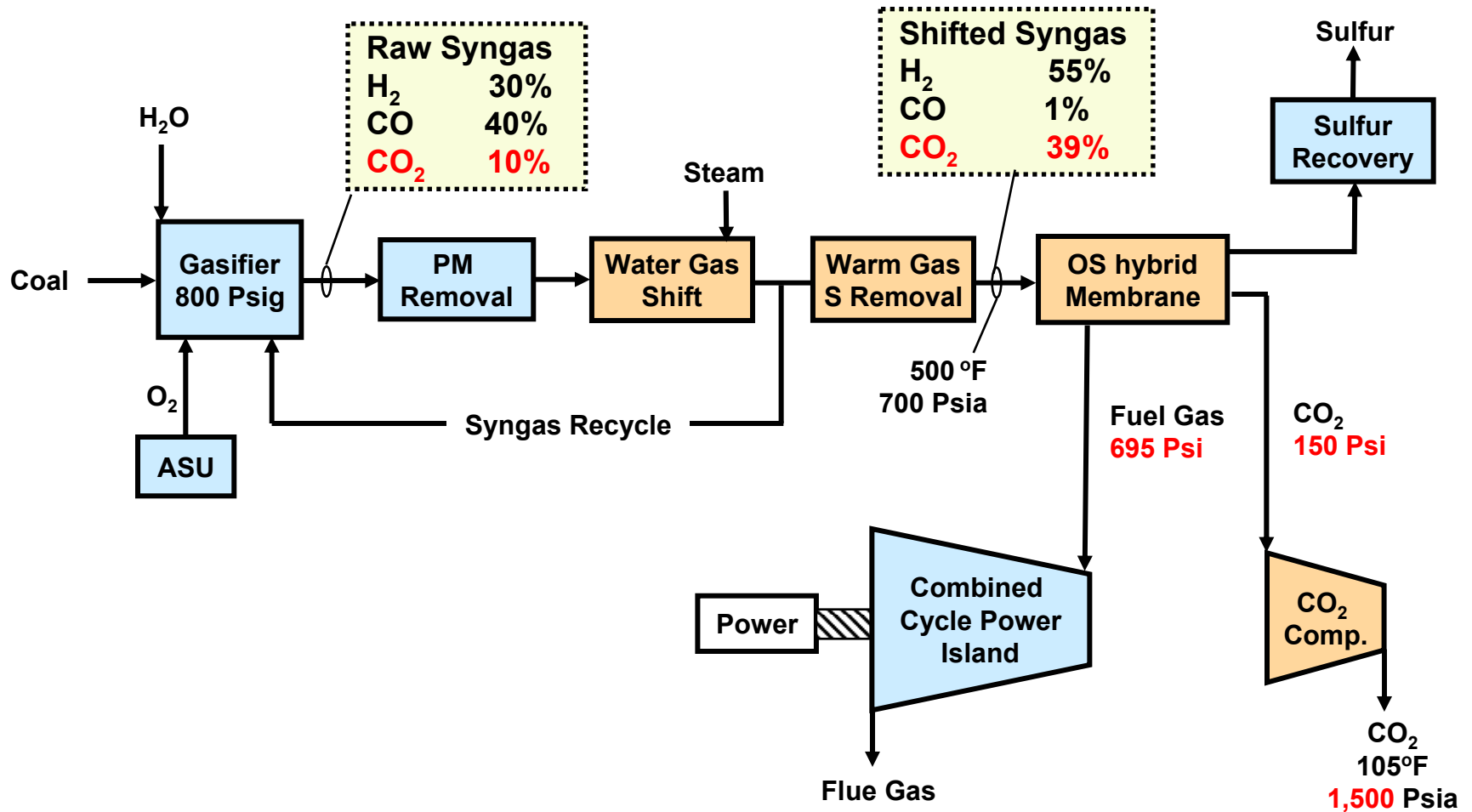


# Membrane CO<sub>2</sub> capture

# Hybrid Membrane for CO<sub>2</sub> Separation in IGCC Power Plants

- 1. Trade-off between reduced CO<sub>2</sub> compression load and H<sub>2</sub> product loss**
  - CO<sub>2</sub> exits separator at **150** psi compared to **50** psi for Selexol,
  - but up to 5% of hydrogen product is lost through the membrane
- 2. Linked with warm gas SO<sub>2</sub> capture, can avoid cooling and reheating fuel gas**
  - Membrane stable between 300-570°F
- 3. Reduced operating & maintenance costs associated with membranes versus liquid circulation**

# IGCC with Membrane CO<sub>2</sub> Capture



# More Detailed Look at the Membrane

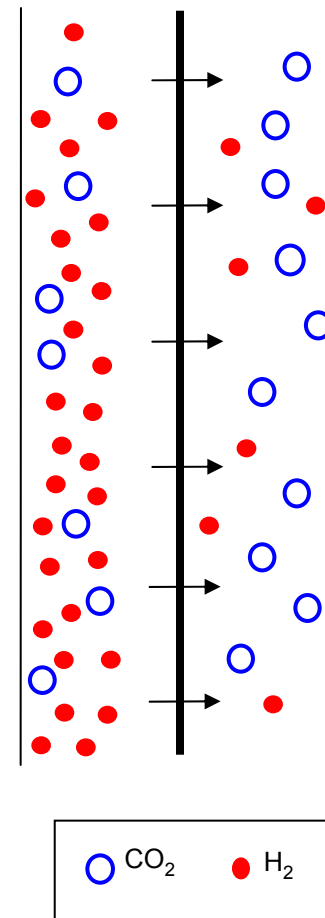
*Selectivity – ratio of permeances (P)*

*This case is reverse selectivity*

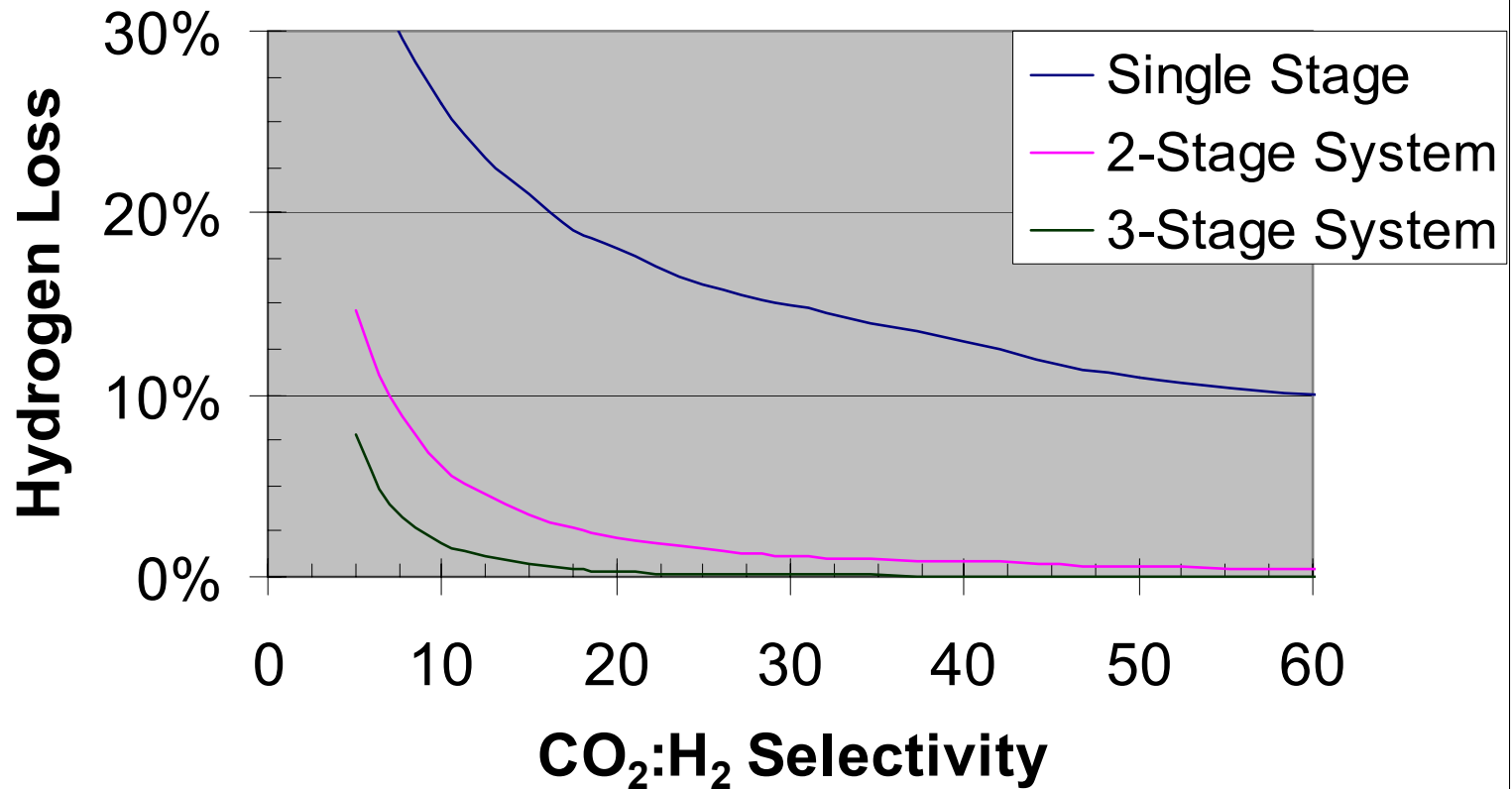
$$P_{CO_2} / P_{H_2} > 1$$

*The CO<sub>2</sub> product is the permeate*

$$\text{Molar flux} = \text{Permeance}_n \cdot \Delta p_{p_n}$$

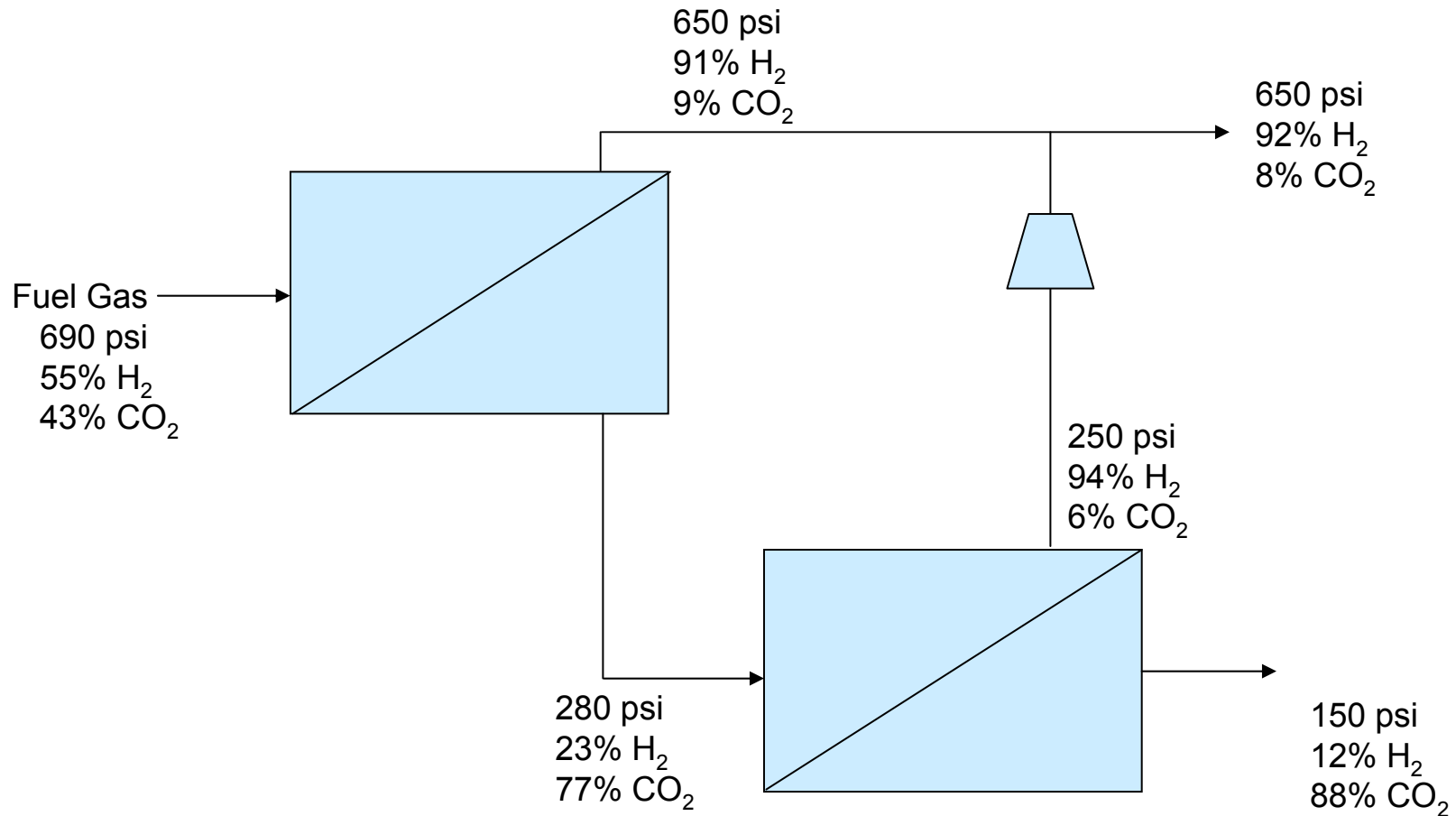


## Organosilane Membrane Performance (simple, 2-species flux model)



# 2-stage membrane separation process

## 13:1 selectivity



# Assumptions for Membrane Systems Analysis

- **CO<sub>2</sub> / H<sub>2</sub> Selectivity, 13:1**
- **Membrane cost, 400 \$/m<sup>2</sup>**
- **Membrane life, 2 years**
- **Maximum trans-membrane pressure difference 400 psi**



# Future Work for the Organosilane Membrane Project

- Increment membrane model
- More rigorous model of warm sulfur removal
- Identify technology for recovery of residual H<sub>2</sub>
- Explore niche applications

# Future Work

- **Finish current analyses**
  - AA (absorption temp, ammonia slip, mercury)
  - Membrane (warm S, increment model, pp driver)
  - Aminated sorbent (pressure drop, kinetics)
  - Lithium sorbent (lower temp, integration with shift)
- **Hand off promising technologies for more detailed modeling**
- **Assess additional technologies**
  - Water hydrate
  - Pressure swing absorption
  - solid sorbents

# Key Assumptions

<b>Capital Charge Factor (%)</b>	<b>14.5</b>
<b>Dollars (Constant)</b>	<b>2002</b>
<b>Plant Life (Years)</b>	<b>20</b>
<b>Coal Cost (\$/ton Illinois #6)</b>	<b>28</b>
<b>Power plant Capacity Factor (%)</b>	<b>65</b>
<b>Pipeline Distance (miles)</b>	<b>50</b>
<b>Saline Injection Pressure (psia)</b>	<b>1,500</b>